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# PATENT SPECIFICATION

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## (54) PROCESS FOR MAKING CHLOROPRENE-SULFUR COPOLYMERS

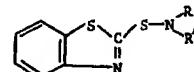
(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for making chloroprene - sulfur copolymers having improved flex-resistance, and tear strength after aging.

Chloroprene-sulfur copolymers, sometimes referred to as sulfur-modified chloroprene polymers, have been commercially available for many years and have enjoyed wide acceptance as versatile elastomers having good resistance to oils, solvents, and greases. Such chloroprene polymers are prepared by polymerizing chloroprene in an aqueous emulsion in the presence of a free radical catalyst and elemental sulfur. Despite the already superior properties of the resulting polymers, still further improvements are constantly being sought. Two significant properties that have an effect upon the use to which chloroprene polymers can be put are flex resistance, and tear strength after aging. Improvements in these properties result in a chloroprene polymer that can be fabricated into articles used in applications in which the article is subjected to stress and high temperatures, such as in V-belts and mining cables, requiring good flex resistance and tear strength.

It has now been found that chloroprene-sulfur copolymers having improved flex resistance and tear strength after aging can be prepared if there is present in the polymerization system particular sulfenamides. More particularly, the present invention is directed to a process for making chloroprene-sulfur copolymers which comprises polymerizing chloroprene in an alkaline aqueous emul-

sion in the presence of elemental sulfur and free radical polymerization catalyst to form a polychloroprene latex and introducing into the system at a time no later than when the polymer is in the latex state at least 0.5 parts by weight per hundred parts organic monomer of a sulfenamide compound having the structure



where R and R' are independently alkyl, cycloalkyl or aralkyl radicals any of which may contain substituents which do not detrimentally affect polymerization or one of R or R' is hydrogen, or R and R' together with the nitrogen atom to which they are attached form a saturated ring. It is necessary to add the sulfenamide to the system no later than when the polymer is in the latex state. Generally, the sulfenamide is added to monomer before polymerization is initiated, or it is added after polymerization has been terminated but while the polymer is still in the latex state. The sulfenamide can also be added to the latex during polymerization. In order to realize the beneficial effects in relation to flex resistance and tear strength at least 0.5 parts by weight per hundred parts monomer of the sulfenamide is added. Preferably, the process includes the additional step of subsequently adding a suitable peptizing agent to the chloroprene polymer latex.

The polymerization of chloroprene-sulfur copolymers is carried out in a conventional manner, except for the presence of certain sulfenamides. Polymerization may be conducted in an aqueous emulsion using a free radical polymerization catalyst, e.g., water-soluble alkali metal or ammonium ferricyanides and peroxy compounds such as alkali metal or ammonium persulfates, hydrogen peroxide, cumene hydroperoxide, and dibenzoyl perox-

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ide, and elemental sulfur at temperatures between 0° and 80°C., generally between 40° and 50°C. As is well known in the art, polymerization can be carried to a predetermined desired degree and stopped by use of conventional "short-stopping" agents. Generally, monomer conversion is from 50 to 98%. According to the present invention the benzothiazolesulfenamide is introduced into the system at a time no later than when the polymer is in the latex state. Preferably, the invention includes the additional step of subsequently adding a peptizing agent to the polymer latex.

Benzothiazolesulfenamides having the structure illustrated in the formula above are used in the process of this invention. The sulfenamides are always added to the system under non-curing conditions. The substituents represented by R and R' in the formula are alkyl, cycloalkyl, or aralkyl radicals and one of R or R' can be hydrogen, or R and R' taken together can form a saturated ring with the nitrogen.

The number of carbon atoms in the alkyl, cycloalkyl, or aralkyl radicals is not critical and the upper limit is a matter of practical considerations. These radicals are preferably hydrocarbon radicals, although they may contain substituents which do not detrimentally affect polymerization. Generally, alkyl radicals will contain one to 12 carbon atoms. The cycloalkyl radicals will usually contain 5-7 carbon atoms, although polycyclic rings can be used containing up to 12 carbon atoms. The aralkyl radicals that are used are those in which an aryl radical, preferably phenyl, is attached to the alkyl or a cycloalkyl radical. The cycloalkyl radicals can be substituents on the alkyl radicals or the cycloalkyl radicals can be substituted with alkyl radicals or other cycloalkyl radicals. Representative examples of suitable NRR' radicals of the above type include diethylamino, dimethylamino, diisopropylamino, tert-butylamino, octylamino, (1-ethylcyclohexyl)amino, cyclohexylcyclopentylamino, (1,1,3,3-tetramethylbutyl)amino, dodecylamino, benzylamino, ( $\alpha$ -methylbenzyl)amino, and diphenethylamino.

When the —NRR' of the above formula forms a saturated ring, it may be morpholine or a saturated ring containing only carbon and hydrogen in addition to the nitrogen. In general, each ring will contain 5 to 7 members, including the nitrogen although polycyclic rings may contain, for example, up to 12 members. The rings may be substituted with hydrocarbon radicals, particularly with alkyl, cycloalkyl, or aryl hydrocarbon radicals containing up to 6 carbon atoms. Representative examples of radicals of the type in which —NRR' is part of a cyclic structure are morpholino (i.e., 4-morpholinyl), 2,6-diethyl-morpholino, 3,5-dimethylmorpholino, piperidino (i.e., 1-piperidyl), pyrrolidinyl, hexahydro-1-azepinyl, 3-azabicyclo-[3.2.0]hept-3-yl, and 3-azabicyclo[3.2.2]non-3-yl. The preferred sulfenamide used in the process of this invention is 2-(morpholinothio)benzothiazole because of its ready availability and over-all effectiveness.

The amount of benzothiazolesulfenamide present in the polymerization system is at least 0.5, preferably 1.5 to 4 parts per hundred parts of monomer. At least 0.5 part is needed to have the desired effect on the flex resistance and tear strength properties of the polymer; in general, no more than 10 parts per hundred parts monomer is required. If the sulfenamide is added to the latex after polymerization, a contact time of at least an hour is adequate before isolation of the polymer.

The sulfenamide can be an ingredient in the original chloroprene emulsion. Alternatively, it can be added to the polymerization system at the termination of polymerization. Polymerization can be terminated by adding a conventional so-called "short-stopping" agent, such as those described, for example, in U.S. Patent 2,576,009. If a "short-stopping" agent is added to terminate polymerization, the sulfenamide can be incorporated as an ingredient in the emulsion containing the short-stopping agent composition, or it can be added separately either before or after polymerization has been stopped. When the sulfenamide is added to the latex, standard techniques for adding compounding ingredients to latex are followed, as described, for example in "Neoprene Latex," by Carl, Elastomers Chemicals Department, E. I. du Pont de Nemours and Company, 1962, pages 125-132. A convenient method is to add the sulfenamide as an aqueous emulsion of a solution of the sulfenamide in toluene as illustrated hereinbelow in Example 1.

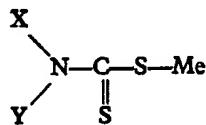
If polymerization is to be stopped at less than about 98% monomer conversion, arresting of polymerization is effected by the addition of a short-stopping agent to the latex that does not react with the sulfide linkages of the chloroprene-sulfur copolymer. Free radical scavengers, that is, compounds that destroy the free radicals present in the polymerization system, are especially effective. Representative free radical scavengers include phenothiazine, dihydric phenols, aralkyl derivatives thereof, and phenolic antioxidants substituted in at least one position ortho to the hydroxy group with a branched alkyl group containing 3-12 carbon atoms. Representative examples are hydroquinone, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylyhydroquinone, 4-tert-butylypyrocatechol, 4,4'-thiobis(6-tert-butyl-o-cresol), 4,4'-methylenebis(2,6-di-tert-butylphenol), 2,6-di-tert-butyl- $\alpha$ -(methylamino)-p-cresol, 4,4'-thiobis(6-

tert - butyl - m - cresol), and 2,6 - di - tert butyl - 4 - phenylphenol.

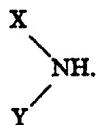
The amount of sulfur used in the polymerization process is ordinarily 0.025—2.5% based on the weight of organic monomer. The particular amount of sulfur employed will depend on the amount of sulfur desired in the polymer chain. The number of sulfide linkages incorporated in the polymer, will, in general, be proportional to the amount of sulfur present in the polymerization system and the number of intralinear sulfide linkages will determine the degree to which the molecular weight can be decreased by cleavage of the sulfide linkages with a peptizing agent. The preferred amount of sulfur present in preparing the polymers of this invention is from 0.3—0.6 part per hundred parts of monomer.

Preferably, the chloroprene polymer is subsequently peptized while in latex form. The peptizing agent is added to the polymeric latex after polymerization is terminated. Suitable peptizing agents that are employed in the process of this invention are dialkyl xanthogen disulfides, water-soluble salts of alkyl xanthic acids, or water-soluble salts of dialkyl dithiocarbamic acids, the last being preferred because of the superior properties imparted to the final vulcanizates. It is believed that these peptizing agents act as catalysts for a reaction by which the sulfenamide is converted to a mercaptobenzothiazole derivative. This derivative, in turn, is believed to react to cleave the intralinear sulfide linkages of the polymer and incorporate benzothiazole structures as terminal groups.

The water-soluble salts of dialkyldithiocarbamic acids may be represented by the structure



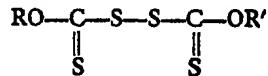
wherein X and Y are alkyl or cycloalkyl groups containing 1—8 carbon atoms or together X and Y can form a saturated ring containing 5—7 members in the ring, including the nitrogen, and Me is a sodium, potassium, or ammonium cation or the cation of an amine



Representative examples of water-soluble salts of dialkyldithiocarbamic acids include sodium dimethyldithiocarbamate, sodium diethyldithiocarbamate, sodium 1 - piperidine -

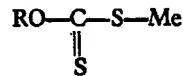
carbodithioate, potassium dibutyldithiocarbamate, sodium cyclohexylethyldithiocarbamate, dibutylammonium dibutyldithiocarbamate, diethylammonium diethyldithiocarbamate, and piperidinium 1 - piperidinocarbodithioate. Preferably, the peptizing agents are water soluble, e.g. sodium, salts of dialkyldithiocarbamates containing 1—4 carbon atoms in each alkyl radical, for example water-soluble salts of dibutyldithiocarbamic acid.

The dialkyl xanthogen disulfide peptizing agents can be represented by the structure:



wherein R and R' are alkyl radicals having 1—8 carbon atoms. Examples of suitable alkyl radicals are methyl, ethyl, propyl, isopropyl, and the various isomeric butyl, amyl, hexyl, heptyl, and octyl radicals. The preferred dialkyl xanthogen disulfides are those in which each alkyl radical has 1—4 carbon atoms, especially diethyl xanthogen disulfide.

The water-soluble salts of alkyl xanthic acids can be represented by the structure:



wherein R is an alkyl radical of 1—8 carbon atoms, and Me is a sodium or potassium cation.

The peptizing agents may be used in the process in amounts ranging from 0.1—5 parts by weight per hundred parts of organic monomer and preferably in amounts from 0.25—3 parts. After the peptizing agent has been added to the latex, said latex is allowed to stand until the desired degree of peptization is obtained. Peptization may be carried out at temperatures between 10° and 50°C. and usually is complete in one hour to 24 hours as evidenced by measurement of Mooney viscosity.

The concentration of organic monomer present in the starting emulsion can vary within a wide range. In general, 30 to 55% by weight, based on the total weight of the emulsion, is the range of concentrations of organic monomer used in the preparation of the polymer. It is to be understood that up to 50% of the chloroprene can be replaced by another copolymerizable monomer. Representative comonomers that can be used in the process include vinyl aromatic compounds, such as styrene, the vinyl toluenes, and vinyl naphthalenes; aliphatic conjugated diolefin compounds such as 1,3 - butadiene, isoprene, 2,3 - dimethyl - 1,3 - butadiene, and 2,3 - dichloro - 1,3 - butadiene; vinyl ethers, esters, and ketones, such as methyl vinyl ether, vinyl

5 acetate, and methyl vinyl ketone; esters, amides, and nitriles of acrylic and methacrylic acids, such as ethyl acrylate, methyl methacrylate, methacrylamide, and acrylonitrile.

10 Conventional emulsifying agents employed in chloroprene polymerization processes are used in the present process for preparing the monomer emulsion and include the water-soluble salts, particularly the sodium, potassium, or ammonium salts of compounds of the following types: long-chain fatty acids; rosins, or rosin derivatives, such as wood rosin, tall oil rosin, disproportionated rosins, or partially polymerized rosin; higher alcohol sulfates; and arylsulfonic acids such as alkylbenzenesulfonic acids, and the condensation product of formaldehyde with a naphthalene-sulfonic acid.

15 If polymerization is stopped at less than about 98% conversion, unreacted monomer can be removed by conventional procedures such as, for example, turbannular steam stripping as disclosed in U.S. Patent 2,467,769.

20 The polymers prepared by the process of this invention may be isolated by standard techniques. For example, the pH can be adjusted to 5.5-6 and the polymer can then be coagulated by freezing in thin layers, as described in U.S. Patent 2,187,146.

25 The chloroprene polymers prepared according to this invention, when vulcanized, i.e., cured and compounded, by conventional techniques, for example, methods described in "The Neoprenes," 1963, by Murray and Thompson, E. I. du Pont de Nemours and Company, or in Du Pont Chemicals for Elastomers Bulletin No. 63, NA-101, show a significant increase in flex resistance and tear strength after aging as compared with polymers prepared without the addition of the sulfenamides.

30 For a clearer understanding of the invention, the following specific examples are given as being illustrative.

35 Example 1.

40 A chloroprene polymer is prepared by polymerizing an aqueous emulsion of chloroprene monomer using the following recipe:

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50	Parts by weight
Chloroprene	100
Nancy wood rosin	4
Sulfur	0.3
Water	126
Sodium hydroxide	0.7
Sodium salt of condensate of formaldehyde and a naphthalene-sulfonic acid ("Lomar" PW, Nopco Chemical Co.;	0.7
60 "Lomar" is a registered Trade Mark)	
Copper ion (added as copper sulfate)	0.00004

Polymerization is carried out at 40°C to a monomer conversion of about 72% by the addition of a catalyst which is a 5% aqueous solution of potassium persulfate containing about 0.125% sodium 2-anthraquinonesulfonate.

Polymerization is stopped by adding 7.25 parts of an emulsion which provides about 2 parts of 2-(morpholinothio)benzothiazole per 100 parts of monomer. The emulsion is prepared from the following components:

	Parts by weight	80
2-(morpholinothio)benzothiazole	2.75	
4,4'-thiobis(6-tert-butyl-o-cresol)	0.11	
Ethyl Antioxidant 736)		
Water	2.79	
Toluene	3.87	85
Sodium lauryl sulfate	0.39	
Sodium salt of condensate of formaldehyde and a naphthalene- sulfonic acid.	0.08	

After the addition of the short-stopping agent, i.e., 4,4'-thiobis(6-tert-butyl-o-cresol), 0.7 part of sodium dibutyl-dithiocarbamate is added as a 23.5% solution in water.

The unreacted monomer is removed, the pH of the latex is adjusted to about 5.6 with acetic acid, and the polymer is isolated on a freeze drum, as described in U.S. Patent 2,187,146.

For comparison a conventional chloroprene polymer is prepared using the same recipe as shown above except that 0.6 part of sulfur is used. Polymerization is carried out at 40°C to 87-88% monomer conversion. Polymerization is stopped by addition of about 1.64 part of an emulsion containing 27.5% tetraethylthiuram disulfide, 8.7% N-phenyl-1-naphthylamine, and 1.1% of 4,4'-thiobis(6-tert-butyl-o-cresol). After polymerization has been stopped, 0.26 part of sodium dibutylthiocarbamate is added as a 47% aqueous solution.

Samples of the polymers are compounded using the following recipe:

	Parts by weight	115
Polymer	100	
Stearic acid	0.5	
N-Phenyl-1-naphthylamine	2	
Magnesia	4	
Medium thermal carbon black	100	120
Naphthenic oil ("Circo" Light Rubber Process Oil, Sun Oil Co.)	10	
Paraffin	1	
Zinc oxide	5	
Accelerator		125

Samples of the compounded stock are cured in a mold under pressure for 30 minutes at 153°C. The tear strength is measured by ASTM Method D 470-71, Section 7.6.

	Flex resistance is measured by ASTM Method D 813-59 and is reported as the number of flexes required to reach a crack length of 0.5 inch.	$T_B$ — Tensile strength at break, psi	10
		$E_n$ — Elongation at break, %	
		The following accelerators are used	
		A None	
5	Tensile properties are measured by ASTM Method D 412-64 T.	B 0.5 part 2 - mercapto - 2 - imidazoline	
	Table I shows the results of the testing. The following abbreviations are used	C 0.4 part tetramethylthiourea	15
	$M_{200}$ — Modulus at 200% elongation, psi	I and the conventional polymer is designated as II.	

TABLE I

Accelerator	A	A.	B	B	C	C
Polymer	I	II	I	II	I	II
Tear strength, lbs./in.						
Original	78	62	69	45	75	48
Aged 3 days at 100°C	68	32	70	26	71	28
Flex resistance flexes to 0.5 in.	$1.26 \times 10^6$ (a)	$0.53 \times 10^6$	$0.23 \times 10^6$	3000	$0.53 \times 10^6$	3600
Tensile properties						
$M_{200}$	1100	1060	1140	1240	1000	1140
$T_B$	1900	1600	1760	1740	1800	1680
$E_B$	500	430	460	400	480	390

(a) At end of test crack had grown to only 0.37 inch

20 It can be seen from the above table that the experimental polymers retain excellent tear strength and flex resistance after curing with conventional accelerators whereas the conventional polymers decrease significantly in both tear strength and flex resistance.

25 Example 2.

The same recipe for the chloroprene emulsion described above in Example 1 is used except that 0.6 part of sulfur is used. Conversion is carried to 85-88%. The latex is divided in half and one portion is stabilized with the same emulsion as used in Example 1 except that Sample A received 2 parts

and Sample B receives 4 parts per hundred parts of monomer of 2-(morpholinothio) benzothiazole. To each sample is then added 0.5 parts of sodium dibutylthiocarbamate. The latexes are aged at ambient temperature (25-30°C) for 6 hours and the unreacted monomers are removed. The polymers are then isolated as in Example 1. The Mooney viscosities of the isolated polymers are about 26.

Samples of the polymers are compounded and cured without accelerators, in the same manner as shown in Table I, column A.

The results are shown in Table II.

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Polymer	A	B	Conventional Polymer (same as Example 1)
Tear Strength, lb./in. Original	75	78	69
Aged 3 days at 100°C.	78	64	43
Flex resistance Flexes to 0.5 in.	$1.26 \times 10^6$ (a)	$1.26 \times 10^6$ (b)	$8.15 \times 10^5$
<b>Tensile Properties</b>			
M <sub>200</sub>	800	625	900
T <sub>B</sub>	1650	1450	1500
E <sub>B</sub>	510	550	460

(a) At end of test crack had grown to only 0.16 inch

(b) At end of test crack had grown to only 0.13 inch

**Example 3.**

5 A series of polymers is prepared using the same recipe and procedure as described above in Example 1 except that different sulfenamides are used as shown below:

		Parts by weight
A.	2-(cyclohexylaminothio)- benzothiazole	2
10 B.	2-(tert-butylaminothio)- benzothiazole	2
C.	2-(2,6-dimethylmorpholinothio)- benzothiazole	2

15 Samples of the polymer are compounded and cured as in Example 1 using 0.5 part of 2-mercapto-2-imidazoline as the accelerator. Table III shows the tear strengths of the vulcanizates.

TABLE III

Tear Strength lbs./in.

	Original	Aged, 3 days at 100°C.
A	42	35
B	65	45
C	72	48
D*	52	27

\* Conventional polymer prepared essentially as described in Example 1 except no sulfenamide was added to the latex.

**Example 4.**

This example illustrates polymerization in the presence of the sulfenamide. The recipe of the monomer emulsion is as follows:

Chloroprene	100	20
Nancy wood rosin	4	25
2-(morpholinothio)benzothiazole	4	
Sulfur	0.35	
Water	124.2	
Sodium hydroxide	0.7	
Sodium salt of condensate of formaldehyde and a naph- thalenesulfonic acid	0.7	30

Polymerization is carried out at 40°C. using the same catalyst as in Example 1. The polymerization is stopped at about 80% monomer conversion by addition of an emulsion composition containing about 0.015 part each of phenothiazine and 4 - tert - butylpyrocatechol and 0.17 part of 2,6 - di - tert - butyl - 4 - phenylphenol. After cooling to 25°C., 0.7 part of sodium dibutyldithiocarbamate is added. The latex is allowed to stand overnight and isolated as in Example 1. The Mooney viscosity (ML 1+2.5/100°C.) of the isolated polymer is 68.

The polymer is compounded using the following recipe:

	Parts
Polymer	100
Stearic acid	0.5
Octylated diphenylamine ("Octamine", Uniroyal)	2
Magnesia	4
Semi-reinforcing furnace black	23
Medium thermal carbon black	127

Aromatic oil ("Sundex" 790, Sun Oil Co.)	Parts 20	Samples are cured and tested as in Example 1. Table IV shows the results of test- ing.	5
Zinc oxide	5		

TABLE IV

	Experimental Polymer	Conventional Polymer (same as Example 1)
Tear strength, lbs./in.		
Original	53	31
Aged 3 days at 100°C	43	31
Flex resistance		
Flexes to 0.5 in.	$2.3 \times 10^5$	900
Tensile Properties		
M <sub>200</sub>	1460	1625
T <sub>B</sub>	1975	1775
E <sub>B</sub>	320	240

## Example 5.

10 The procedure and ingredients described in Example 2 is repeated using 0.6 part of sulfur per hundred parts of monomer. However, polymerization is stopped by adding 1.86 part of an emulsion containing about 1% 15 each of phenothiazine and 4 - tert - butylpyrocatechol and about 27% of 2,6 - di - tert - butyl - 4 - phenylphenol. After polymerization is stopped 1.76 part of 2-(morpholinothio)benzothiazole is added (as a solution in toluene). The isolated polymer has

20 a Mooney viscosity of 177.

Samples of this polymer are compounded and used as in Example 1 using 0.6 part of tetramethylthiourea as the accelerator. One part of sodium diethyldithiocarbamate is added to the curing recipe for the experimental polymer to facilitate milling. Table V shows the tear strengths of the vulcanizate as compared with those of a conventional polymer prepared substantially as described in Example 1 but without sulfenamide.

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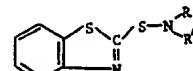
TABLE V

Tear Strength, lbs./in.	Experimental Polymer	Conventional Polymer
Original	70.6	53.8
After 3 days at 100°C.	71.8	32.8

## WHAT WE CLAIM IS:—

1. A process for making chloroprene-sulfur 35 copolymers which comprises polymerizing chloroprene in an alkaline aqueous emulsion in the presence of a free radical polymerization catalyst and elemental sulfur to form a polychloroprene latex and introducing into 40 the system at a time no later than when the polymer is in the latex state at least 0.5 parts by weight per hundred parts organic

monomer of a sulfenamide compound having the structure



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where R and R' are independently alkyl, cycloalkyl or aralkyl radicals any of which may contain substituents which do not detri-

mentally affect polymerization or one of R or R' is hydrogen, or R and R' together with the nitrogen atom to which they are attached form a saturated ring.

5. 2. A process according to claim 1 wherein said sulfenamide is added to monomer before polymerization.

3. A process according to claim 1 wherein said sulfenamide is added to the latex during polymerization.

10. 4. A process according to claim 1 wherein said sulfenamide is added after polymerization but while the polymer is still in the latex state.

15. 5. A process according to any of the preceding claims wherein R and R' are alkyl radicals having 1 to 12 carbon atoms and one of R and R' can be hydrogen.

6. A process according to any of claims 1-4 wherein R and R' are cycloalkyl radicals having 5-7 carbon atoms and one of R or R' can be hydrogen.

7. A process according to any of the preceding claims wherein R and R' are unsubstituted hydrocarbon radicals and one of R or R' can be hydrogen.

20. 8. A process according to any of claim 1-4 wherein the sulfenamide is 2-(morpholiniothio)benzothiazole.

25. 9. A process according to any of claims 1-4 wherein the sulfenamide is 2-(2,6-dimethylmorpholiniothio)-benzothiazole.

30. 10. A process according to claim 6 wherein the sulfenamide is 2-(cyclohexylaminiothio)-benzothiazole.

35. 11. A process according to claim 5 wherein the sulfenamide is 2-(tert-butylaminiothio)-benzothiazole.

40. 12. A process according to any of the preceding claims wherein the amount of said sulfenamide added is from 0.5-10 parts by weight per hundred parts of monomer.

45. 13. A process according to claim 12 wherein the amount of said sulfenamide added is from 1.5 to 4 parts by weight per hundred parts of monomer.

50. 14. A process according to any of the preceding claims wherein the amount of elemental sulfur employed is from 0.025-2.5% by weight of organic monomer.

15. A process according to claim 14 wherein the amount of elemental sulfur em-

ployed is from 0.3 to 6.0% by weight of organic monomer used.

16. A process according to any of the preceding claims comprising the additional step of subsequently adding a peptizing agent to the polymer latex.

17. A process according to claim 16 wherein said peptizing agent is a water-soluble salt of a dialkyl-dithiocarbamic acid, a dialkyl xanthogen disulfide, or a water soluble salt of an alkyl xanthic acid.

18. A process according to claim 17 wherein the peptizing agent is a water-soluble salt of diakyl-dithiocarbamic acid each alkyl group of which contains 1 to 4 carbon atoms.

19. A process according to claim 18 wherein the peptizing agent is a water-soluble salt of dibutyl-dithiocarbamic acid.

20. A process according to claim 17 wherein the peptizing agent is a dialkyl xanthogen disulfide each alkyl group of which contains 1 to 4 carbon atoms.

21. A process according to any of claims 16-20 wherein from 0.25 to 3 parts by weight of said peptizing agent is employed per hundred parts of organic monomer.

22. A process according to any of the preceding claims wherein up to 50% of the chloroprene is replaced by another copolymerizable organic monomer.

23. A process according to any of the preceding claims wherein a free radical scavenger is added to the latex to terminate polymerization.

24. A process according to any of the preceding claims wherein the polymer is vulcanized.

25. A process according to claim 1, substantially as hereinbefore described.

26. A process according to claim 1, substantially as hereinbefore described with reference to any of the Examples.

27. The copolymer product of the process claimed in any of the preceding claims.

28. The copolymer product of any of claims 21-24 as appendent to claims 18 and 8.

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